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21.1 Introduction

In general, finite field DFT and TDDFT calculations yield accurate values for the response properties of molecular systems when standard approximations for the exchange-correlation functionals are used [Gross 1996]. In combination with their high efficiency, this makes these theoretical approaches ideal candidates for the calculation of physical properties of large molecular systems of technological interest. For an important class of materials, however, this potential is not yet realized. It has been observed that density functional calculations on the static response properties of long π-conjugated molecular chains give large overestimations for the polarizability [Champagne 1998] when local and gradient-corrected exchange-correlation functionals are used. The errors become even worse for their nonlinear response properties [Champagne 1998]. Similarly, the static polarization of π-conjugated push-pull systems is incorrectly described [Champagne 2000], even if it is obtained in the absence of an external field. Closely related to these findings, also large errors have been reported in the calculated excitation energies [Grimme 2003]. The reason for these deviations is by now well understood: both local and gradient-corrected density approximations are unable to correctly describe the induced contribution to the exact exchange-correlation potential (see Chap. 9). It contains a component that increases linearly along the chain counteracting the external field [van Gisbergen 1999b, Gritsenko 2000]. The density, on the other hand, remains more-or-less periodic in the bulk of the chains, and changes only at the chain ends. The same phenomenon that is responsible for the macroscopic exchange-correlation field in insulating solids [Gonze 1995b, Gonze 1997b, Martin 1997a] seems to be at work here. In the infinite systems this additional screening field can be viewed as a polarization dependent exchange-correlation effect. In the finite molecular systems, however, the complete density is known, and no polarization dependence of the exchange-correlation functional needs to be invoked. It becomes clear that the failure of the standard density functionals is related to their local density dependence: the exchange-correlation potential is relatively insensitive to the polarization charge induced by the external electric field at the chain ends. The external field is insufficiently screened, and a too strong response is obtained in these approximations.

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21.2 The Counteracting Exchange Potential

The overestimation of the polarizability is readily reproduced in finite field calculations on model chains consisting of a coaxial stack of evenly spaced hydrogen molecules. By using the approximation for the exact exchange potential developed by Krieger, Li, and Iafrate (KLI) [Krieger 1992b], the main cause of the occurrence of the counteracting exchange-correlation field could be traced back to the so-called "response" part of this exchange potential [van Gisbergen 1999b, Gritsenko 2000]. Here the KLI potential has two contributions,

$$v_{\mathrm{x}}^{\mathrm{KLI}}(\boldsymbol{r}) = v_{\mathrm{x}}^{\mathrm{hole}}(\boldsymbol{r}) + \sum_{i=1}^{N-1} f_i \frac{n_i(\boldsymbol{r})}{n(\boldsymbol{r})} \,. \tag{21.1}$$

The first term is the potential of the Fermi hole $v_{\mathrm{x}}^{\mathrm{hole}}(\boldsymbol{r})$, which has the correct asymptotic attractive long-range behavior $-1/r$. The second term is the exchange contribution to the "response part", which depends on the Kohn-Sham orbitals via the orbital densities $n_i(\boldsymbol{r})$ and orbital-energy dependent weights f_i. Here deeper-lying orbitals have bigger weights. The response part is repulsive and short-range as it decays exponentially for large r. Surprisingly, it is not the polarization of the long-range Fermi hole part that causes the global change in the potential as was previously proposed to explain the related effect in solids [Gonze 1995b, Gonze 1997b, Martin 1997a]. Instead, the nonlocal density dependence of the counteracting field arises due to the polarization of the occupied orbitals induced by the external field [van Gisbergen 1999b, Gritsenko 2000]. This effect can be understood in the following way. Suppose that in the zero field case we have two molecular orbitals being the bonding and anti-bonding combinations, $\varphi_{\mathrm{b}}(\boldsymbol{r}) = [\phi_1(\boldsymbol{r}) + \phi_2(\boldsymbol{r})]/\sqrt{2}$ and $\varphi_{\mathrm{a}}(\boldsymbol{r}) = [\phi_1(\boldsymbol{r}) - \phi_2(\boldsymbol{r})]/\sqrt{2}$ respectively of two fragment orbitals $\phi_1(\boldsymbol{r})$ and $\phi_2(\boldsymbol{r})$. In the presence of the perturbing field these orbitals will get mixed, leading to predominantly $\phi_1(\boldsymbol{r})$ and $\phi_2(\boldsymbol{r})$ type molecular solutions. Now, assuming that the fragment orbitals are rigid, the total density will not be changed by this mixing, and it remains $n(\boldsymbol{r}) = |\phi_1(\boldsymbol{r})|^2 + |\phi_2(\boldsymbol{r})|^2$. A local density functional will hence not be sensitive to this orbital polarization. Nevertheless, the response part of the KLI potential will be changed as the weights depend on the orbital energies: the weight f_1 will increase for the stabilized orbital having its density $n_1(\boldsymbol{r}) = |\phi_1(\boldsymbol{r})|^2$ at the lower potential side, and f_2 will decrease for the destabilized orbital with the density $n_2(\boldsymbol{r}) = |\phi_2(\boldsymbol{r})|^2$ at the higher side. The net result takes the form of a counteracting field. Even though the response part is of short range, the dependence on the orbitals makes it sensitive to global changes in the molecule.

Similar results have been obtained using an improved x-only approximation based on a physically motivated common energy denominator approximation (CEDA) for the orbital Green's function [Gritsenko 2001, Grüning 2002]. This approximation differs from the KLI approach in the sense that

the occupied-occupied orbital mixing is now completely removed in the corresponding approximation for the density-density response function. The resulting approximation for the exchange potential takes a form similar to the KLI result (21.1), but now it contains also off-diagonal terms,

$$v_{\mathrm{x}}^{\mathrm{CEDA}}(\boldsymbol{r}) = v_{\mathrm{x}}^{\mathrm{hole}}(\boldsymbol{r}) + \sum_{i=1}^{N-1} f_i \frac{n_i(\boldsymbol{r})}{n(\boldsymbol{r})} + \sum_{i,j\neq i}^{N} f_{ij} \frac{\phi_i^*(\boldsymbol{r})\phi_j(\boldsymbol{r})}{n(\boldsymbol{r})} \; . \tag{21.2}$$

This additional off-diagonal orbital structure of the CEDA potential was shown to be important in particular for the description of the response properties of molecular chains [Grüning 2002].

Though these KLI and CEDA functionals resemble many features of the exact exchange-only, or optimized effective potential [Talman 1976, Ivanov 1999, Görling 1999a], the exact exchange-only potential gives results much closer to Hartree-Fock, with a higher counteracting field strength [Mori-Sanchez 2003, Kümmel 2004]. However, even the Hartree-Fock polarizabilities overestimate the values obtained with correlated methods. It remains to be seen to what extent correlation effects contribute to the global counteracting field, as the optimized potential approaches have until recently [Facco Bonetti 2001] been restricted to the exchange-only approximation.

The orbital dependence of these (approximate) exchange-only potentials allows for the nonlocal density-dependence, which is the basis for their success. In the static linear response approach the change in the exchange potential $\delta v_{\mathrm{x}}(\boldsymbol{r})$ is obtained from the density change $\delta n(\boldsymbol{r})$ via the exchange kernel,

$$\delta v_{\mathrm{x}}(\boldsymbol{r}) = \int \mathrm{d}^3 r' \, f_{\mathrm{x}}(\boldsymbol{r}, \boldsymbol{r}') \delta n(\boldsymbol{r}') \; , \tag{21.3}$$

with

$$f_{\mathrm{x}}(\boldsymbol{r}, \boldsymbol{r}') = \frac{\partial v_{\mathrm{x}}(\boldsymbol{r})}{\partial n(\boldsymbol{r}')} \; . \tag{21.4}$$

When the orbital structure of the exchange potential is properly incorporated in the exchange kernel [Gritsenko 2001, Grüning 2002], evidently the same results should be obtained in a response calculation as in the finite field approach. The kernel will have to be nonlocal in order to generate the characteristic contribution counteracting the external electric field. In solids related strategies have been applied. It was shown for several semiconductors that certain excitonic features, which are missing in the calculated absorption spectrum obtained using local functionals, can indeed be described correctly by using the exact-exchange kernel [Kim 2002b, Kim 2002a], or simply by imposing the typical $1/|\boldsymbol{r} - \boldsymbol{r}'|$ long-range dependence of $f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}')$ [Reining 2002, Botti 2004].

A very promising new route to improve upon the exchange-only kernels is found in comparing the TDDFT approach and the related Bethe-Salpeter equation from many-body perturbation theory [Onida 2002, Sottile 2003,

Adragna 2003, Marini 2003b, Stubner 2004]. Using this Bethe-Salpeter approach on, e.g., infinite polyacetylene polymers [Rohlfing 1999a, Puschnig 2002], it has been found that the excitonic features found in solids are present also in these one-dimensional π-conjugated systems.

21.3 An Alternative to Orbital-Dependent Potentials

Another route to include the nonlocal density dependence can be followed by changing to current dependent functionals within the framework of time-dependent current density functional theory [Dhara 1987, Ghosh 1988, Vignale 1996, Vignale 1998] (see Chap. 5). The main motivation here is that the current density can be seen as a local indicator of global changes in the system, and that a local exchange-correlation approximation can indeed be used if the basic variable is the induced current density rather than the density. Such a current functional was derived by Vignale and Kohn [Vignale 1996, Vignale 1998]. The current formulation is inherently a dynamical one, in which static response properties can be obtained in the low frequency limit of the time-dependent perturbation approach. Van Faassen et al. [van Faassen 2002, van Faassen 2003a] showed that including the current functional of Vignale and Kohn in the response calculations gives greatly improved static polarizabilities for several π-conjugated polymers, while the results for the nonconjugate polymers, which are already correctly described within the local density approaches, are modified only to a small extent. Unfortunately, however, in this current functional approach the description of the prototype hydrogen chain remained problematic. This is in great contrast with the (approximate) exchange-only orbital potentials and Hartree-Fock results, which do produce a sizable counteracting field in this model system. Mixed quality results were also obtained for the frequency dependent response of small molecules. The excitation energies were improved upon the ALDA results for $\pi^* \leftarrow \pi$ transitions in several π-conjugated systems, but much worse results were sometimes obtained in other systems [van Faassen 2003b].

Figure 21.1 shows the static axial polarizability per oligomer unit for the prototype π-conjugated system, polyacetylene, obtained using the adiabatic local density (ALDA) and Vignale-Kohn (VK) functionals [van Faassen 2002], together with restricted Hartree-Fock (HF) results [Kirtman 1995], and results from second order perturbation calculations (MP2) [Toto 1995]. Exact exchange-only results are expected to be very close to the HF results [Mori-Sanchez 2003, Kümmel 2004]. It becomes clear that the overestimation of the polarizability observed in the ALDA calculations is reduced considerably by using the VK functional, giving values in close agreement with MP2 results that are somewhat smaller than HF results. The same current functional method can also be applied to the absorption spectrum of the infinite chain of the prototype polyacetylene system [Berger 2005]. This gives results that correspond well with the finite oligomer results [van Faassen 2002, van

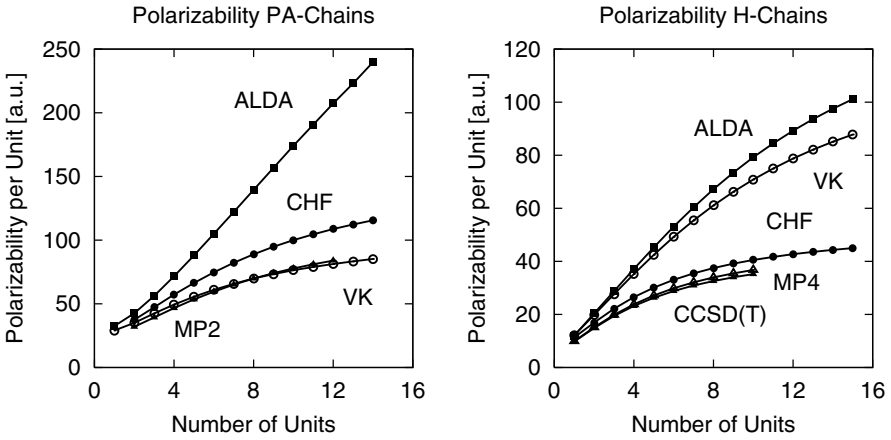

Fig. 21.1. The static axial polarizability per oligomer unit for polyacetylene (*left*) obtained using the adiabatic local density (ALDA) and Vignale-Kohn (VK) functionals [van Faassen 2002], together with spin-restricted coupled Hartree-Fock (CHF) results [Kirtman 1995] and results from second order perturbation calculations (MP2) [Toto 1995]. Similar results for the model hydrogen chains (*right*), now compared with spin-restricted coupled Hartree-Fock (CHF) results, fourth order perturbation calculations (MP4), and coupled cluster calculations with singles, doubles and triples included (CCSD(T)) [Champagne 1995]

Faassen 2003a], but that deviate considerably from Bethe-Salpeter results [Rohlfing 1999a, Puschnig 2002] and experiment. In particular the position of the absorption maximum is shifted upward like in the oligomers [van Faassen 2004] but now too strongly.

One may wonder if the application of the VK functional in molecular systems is justified. After all, the VK functional was derived for the electron gas under the assumption of weak spatial inhomogeneity, which is certainly violated in these systems. However, the VK-functional satisfies a number of important physical constraints which are valid for systems with arbitrary time-dependence and inhomogeneity [Vignale 1996, Vignale 1998]. In fact, the Vignale-Kohn functional can be viewed as the linear regime limit of the exact reformulation of TDDFT in the co-moving Lagrangian frame [Tokatly 2005a, Tokatly 2005b] (see Chap. 8). These exact properties may support the application to molecular systems, but the correctness of the results can not be guaranteed, as the (induced) deformations are certainly not small, and the VK functional is thus applied well beyond the linear regime. The varying quality of the results obtained with this functional for the molecular response properties may also be the result of the following arguments. The functional can be cast as a viscoelastic stress field [Vignale 1997], in which viscoelastic coefficients $\tilde{\eta}_{\rm xc}(n_{\rm GS},\omega)$ and $\tilde{\zeta}_{\rm xc}(n_{\rm GS},\omega)$ enter that are frequency dependent functions of the ground state density, and that are deter-

mined by the longitudinal and transverse response kernels $f_{\mathrm{xc,\,L}}(n_{\mathrm{GS}}, \omega)$ and $f_{\mathrm{xc,\,T}}(n_{\mathrm{GS}}, \omega)$ of the homogeneous electron gas [Vignale 1997]. Even though these kernels have been studied extensively, both their frequency dependence [Gross 1985, Gross 1985, Iwamoto 1987, Conti 1997, Qian 2002], and their static limits [Conti 1997, Qian 2002, Böhm 1996, Nifosì 1998, Conti 1999], are still not known accurately. In particular, this is true for the static limit of the transverse kernel, which determines to a large extent the strength of the screening field, and hence the absorption spectrum [Berger 2005]. The calculated shift of the absorption maximum and also the related static polarizability is strongly dependent on the particular parameterization of the density-dependence that is used for the static transverse electron gas kernel. In the π-systems a different region (π-orbitals) is probed by the response calculation than in the hydrogen chains (σ-orbitals). The different average densities and inhomogeneities involved may explain the different performance for these systems. More accurate electron gas kernels will be needed to verify if the application of the Vignale-Kohn functional to molecular response properties is indeed justified.

21.4 Conclusion

In conclusion, we can state that the strong overpolarization observed in DFT calculations that use local and gradient-corrected density functionals for the exchange-correlation potential is the result of the locality of these functionals. The origin of the nonlocal density dependence of the exact exchange-correlation contribution to the induced Kohn-Sham potential has been established as resulting from a polarization of the occupied Kohn-Sham orbitals, which does not modify the density locally. The nonlocal density dependence of the exchange-correlation potential can be introduced via an explicit orbital dependence either via the optimized potential method or by using expansions in terms of the Kohn-Sham Greens function, or by introducing current density functionals. The results obtained with the various methods are not yet in full agreement. Improved approximate exchange-only potentials, beyond KLI and CEDA, should eventually converge to the exact exchange-only results, which in turn are close to the Hartree-Fock results. Further progress can be made if correlation effects are included in the optimized potential. In the current functional approach more accurate electron-gas kernels have to be obtained, and the regime beyond weak inhomogeneity should be described correctly. This may most elegantly be done using the reformulation of TDDFT in the co-moving Lagrangian frame.